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Reactions of Thiocarbonyl Compounds with Electrophilic and Nucleophilic Carbenes as well as with their Metal Complexes

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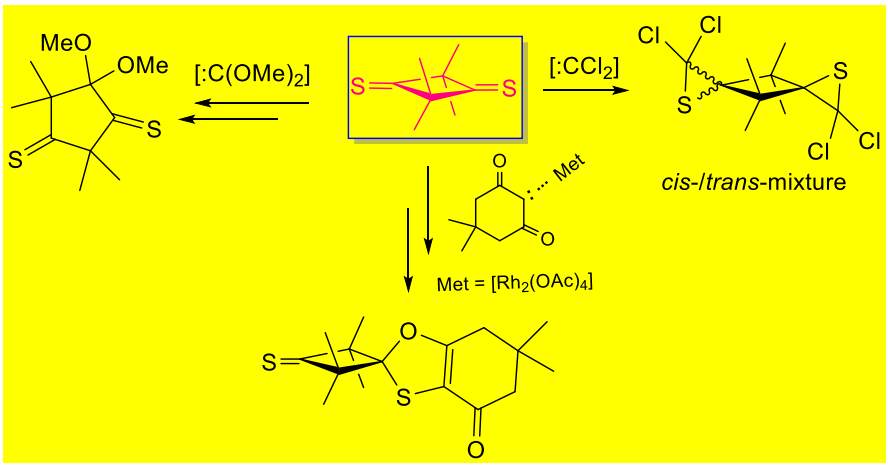
Graphical abstract



Abstract

A variety of cyclic and acyclic products are reported for reactions of thiocarbonyl compounds with carbenes and their metal complexed derivatives. Electrophilic and nucleophilic carbenes react with non-enolizable thioketones yielding thiocarbonyl ylides or 1,3-zwitterions, respectively, as plausible, reactive intermediates. In most cases, the initially formed intermediates undergo 1,3-electrocyclization yielding respective thiiranes, which, depending on the substitution pattern, are either isolated as final products or extrude elemental sulfur forming substituted ethylene derivatives. In addition, reactive thiocarbonyl ylides formed from α-oxo substituted carbenoids after the thiophilic attack onto the C=S bond undergo competitive 1,3- versus 1,5-dipolar electrocyclization leadig to thiiranes or 1,3-oxathioles, respectively. From the point of view of potential practical applications (coordination chemistry, organometallic chemistry,

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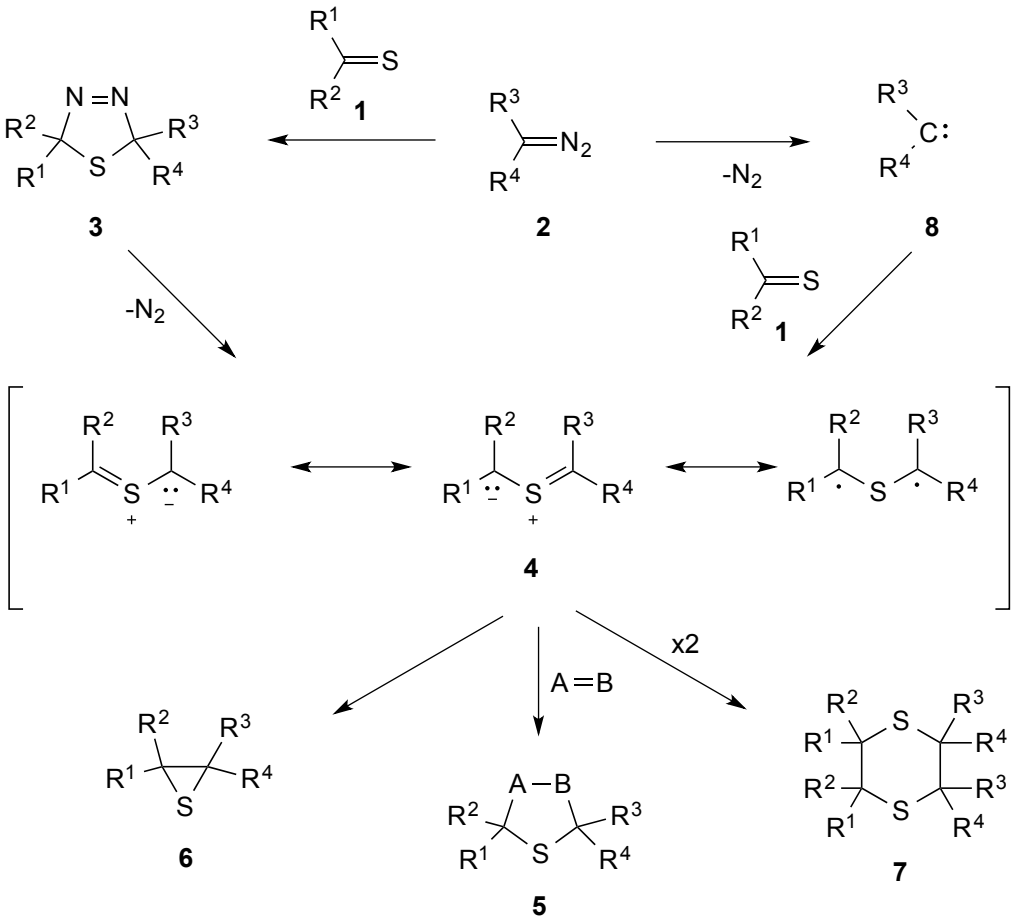
1. Introduction

In the recent three decades, a growing interest in the exploration of diverse thiocarbonyl compounds for the synthesis of more complex products, such as sulfur heterocycles, but also non-cyclic molecules and highly substituted ethenes is observed. Cycloaddition reactions are of special importance as thioketones were recognized as 'super-dipolarophiles' in [3+2] cycloadditions [1–3] and 'super-dienophiles' in hetero-Diels–Alder reactions [4]. Despite of the fact that first reactions of diazomethanes with aromatic thioketones were reported in the 1920s [5,6], their mechanisms leading to thiiranes, 1,3-dithiolanes or 1,4-dithianes were elucidated only 60 years later by Huisgen. He demonstrated that these reactions occur via the initial [3+2]-cycloaddition leading to 1,3,4-thiadiazolines **3**, which smoothly eliminate N_2 to give thiocarbonyl ylides **4** as reactive key intermediates, which govern further inter- or intramolecular conversions [7–10] (Scheme 1). Thiocarbonyl *S*-methanides (thiocarbonyl ylides) are classified in the group of the so-called 'sulfur centered 1,3-dipoles', which cannot be isolated, but in the presence of a suitable dipolarophile are trapped yielding five-membered *S*-heterocycles **5**. Alternatively, they undergo 1,3-dipolar electrocyclization to give thiiranes **6** or dimerize to form 1,4-dithianes **7**. Moreover, in the case of thiocarbonyl ylides containing other functional groups such as carbonyl or amino groups, other heterocyclization reactions can occur.



Scheme 1. Two methods for the generation of thiocarbonyl ylides from thiocarbonyl compounds and diazo compunds, and some of their reactions.

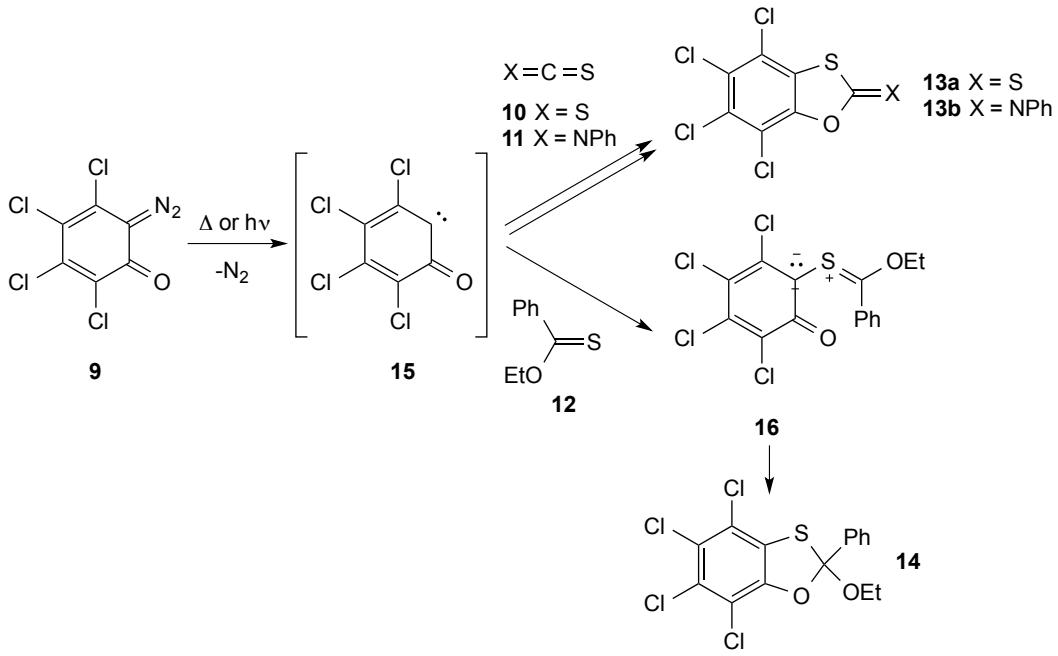
Another method to generate reactive thiocarbonyl ylides comprises the electrophilic attack of a two-valent carbene **8** or carbenoid onto the electron-rich sulfur atom of the C=S group. Diazomethane derivatives are known as the most important source of carbenes/carbenoids, which are formed upon heating, photolysis or by metal-assisted decomposition. It is well established that diazomethanes, functionalized at the α-position with electron withdrawing groups, display reduced reactivity as 1,3-dipoles, and in most cases their reactions with thiocarbonyl groups require the involvement of a catalyst to change the reaction type from the [3+2] cycloaddition to the electrophilic approach of the carbene. The formation of thiocarbonyl ylides can also be achieved when reactive carbenes are generated from other precursors, e.g. dichlorocarbene from chloroform in a two-phase system or by thermal decomposition of Seyfert's reagent ($PhHgCCl_3$).

The goal of the present review is a survey of the reactions of C=S compounds occurring via thiocarbonyl ylides, zwitterionic intermediates or diradicals generated in situ with participation of a carbene/carbenoid as reactive species. Competitive insertion processes into single C−C, C−S, S−S and N−H bonds will also be discussed.

2. Decomposition of less reactive diazo compounds in the presence of a thiocarbonyl derivative

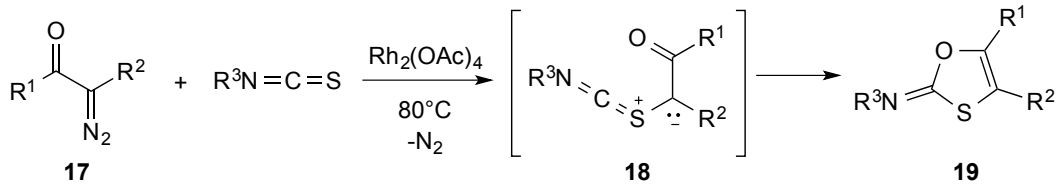
2.1. Intermolecular reactions

In a pioneering work, Huisgen described thermal and photolytical reactions of 6-diazo-2,3,4,5-tetrachlorohexa-2,4-dien-1-one (tetrachloro-*o*-quinonediazide, **9**) with thiocarbonyl compounds **10**–**12**, which led to the corresponding benzoxathioles **13** and **14** [11] (Scheme 2). No reaction mechanism was formulated, but it seems likely that a carbene species **15** added to the C=S groups yielding the corresponding α-oxothiocarbonyl ylide, e.g. **16**. The subsequent 1,5-dipolar electrocyclization leads to the isolated products.



Scheme 2. Formation of 1,3-benzoxathioles from α-oxo diazo compound **9** and thiocarbonyl derivatives.

Isothiocyanates were also reacted with α-diazoketones **17** at 80°C in the presence of $Rh_2(OAc)_4$, which induced the formation of the corresponding carbenoid. The latter added to the C=S group of the isothiocyanates to generate α-oxo thiocarbonyl ylides **18**, which in analogy to **16** cyclized to yield 1,3-oxathioles **19** [12] (Scheme 3).



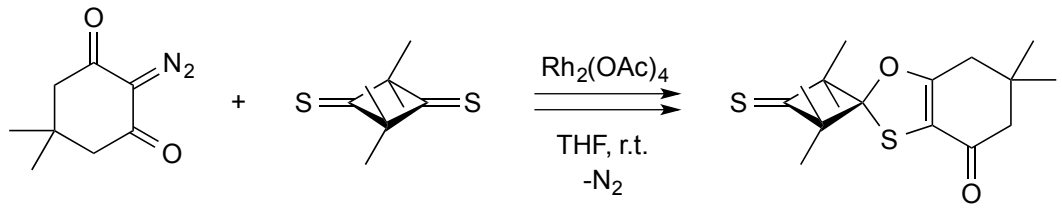
17 **18** **19**

Scheme 3. $Rh_2(OAc)_4$-catalyzed reaction of α-diazoketones **17** with isothiocyanates.

In a recent study, 2-diazocyclohexane-1,3-diones were reacted with aryl isothiocyanates in the presence of a metal catalyst, and $Rh_2(OAc)_4$ was the most efficient one [13]. The only products obtained in high yields (78–93%) were the corresponding 2-arylimino-1,3-oxathiole derivatives.

Analogously, reactions of di(*tert*-butyl)thioketene with allyl α-diazoacetates catalyzed by $Rh_2(OAc)_4$ led to 4-allyl-2-methylene-1,3-oxathiolan-5-ones via 1,5-dipolar electrocyclization of intermediate thiocarbonyl ylides and subsequent Claisen rearrangement [14].

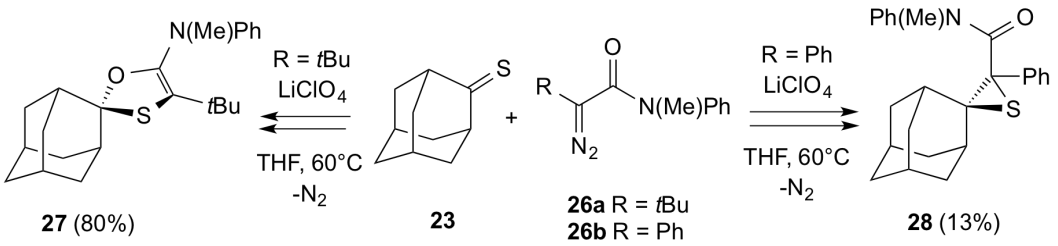
Similary, 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**20**) decomposed in the presence of catalytic amounts of $Rh_2(OAc)_4$ to generate a carbenoid, which added to 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**21**), and the thiocarbonyl ylide formed thereby underwent 1,5-dipolar electrocyclization to give the spirocyclic 1,3-oxathiole **22** [15] (Scheme 4).



20 **21** **22**

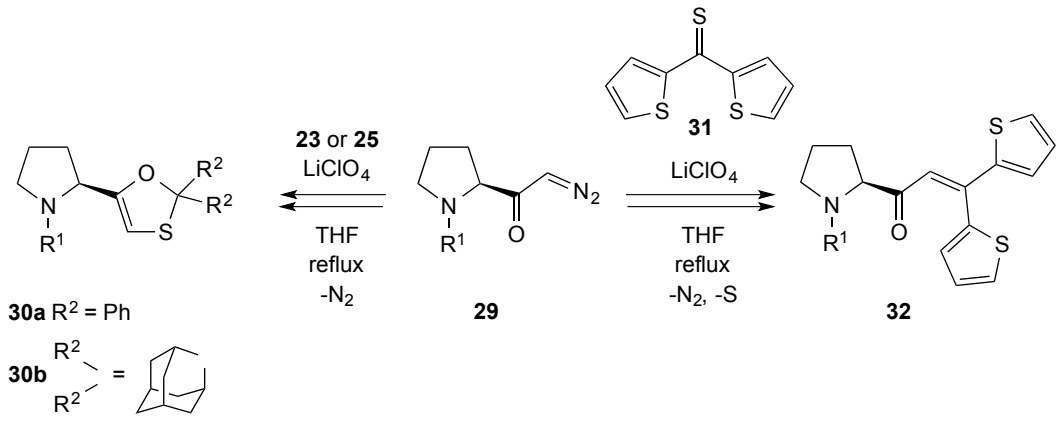
Scheme 4. $Rh_2(OAc)_4$-catalyzed reaction of 2-diazodimedone **20** with cyclobutane-1,3-dithione **21** leading to *spiro*-1,3-oxathiole derivative **22**.

In the same study, reactions of **21** and other thioketones such as adamantanethione (**23**), 3-thioxo-2,2,4,4-tetramethylcyclobutanone (**24**), and thiobenzophenone (**25**) with 2-diazocyclohexanone in THF solution at 50–60°C are also reported. In this series, $LiClO_4$ (10%) was applied as a catalyst. Although the detailed role of this catalyst is not known, most likely its interaction with the α-oxo diazo function results in the formation of a reactive carbenoid-like intermediate, which reacts with a thiocarbonyl group forming the reactive thiocarbonyl ylide. This type of catalysis was applied for the activation of other diazo compounds with reduced reactivity. For example, adamantanethione (**23**) reacts with α-diazoamides **26** in THF at 60°C in the presence of $LiClO_4$, and depending on the substituent R, 1,3-oxathiole **27** or thiirane **28** were obtained as products [16] (Scheme 5).



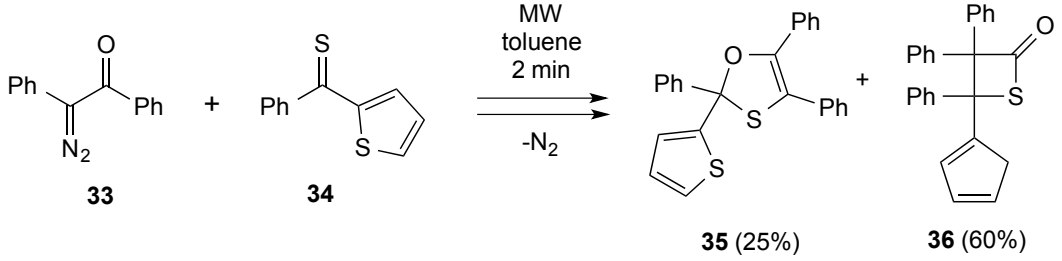
Scheme 5. Reactions of α-diazoamides **26** with adamantanethione (**23**).

Reactions of N-protected (*S*)-diazoproline (**29**) with aryl, hetaryl and cycloaliphatic thioketones were also studied using $LiClO_4$ as a catalyst. Whereas thiobenzophenone (**25**) and **23** yielded 1,3-oxathioles **30**, di(thiophen-2-yl) thioketone (**31**) and other dihetaryl thioketones gave under the same conditions α,β-unsaturated ketones **32** as products of spontaneous sulfur elimination from the intermediate thiiranes [17,18] (Scheme 6). Apparently, the presence of hetaryl substituents in the intermediate thiocarbonyl ylide determines the type of the electrocyclization and, in the case of the 1,3-dipolar electrocyclization to thiiranes, enables the extrusion of sulfur.



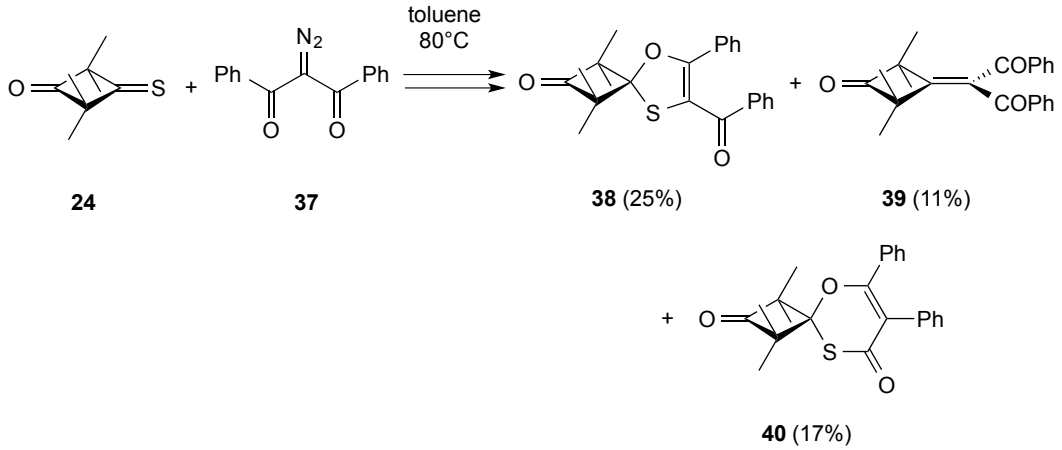
Scheme 6. Different pathways in reactions of (*S*)-diazoprolines **29** with adamantanethione (**23**) (or thiobenzophenone (**25**)) and di(thiophen-2-yl) thioketone (**31**), leading to different products **30a**/**30b** or **32**, respectively.

In contrast to thiobenzophenone (**25**) and other aromatic thioketones, their hetaryl analogues do not react with α-diazoketones neither at standard thermal conditions nor upon $LiClO_4$ catalysis. For that reason, the microwave irradiation was applied to support the formation of a carbene intermediate [19]. For example, the reaction of 2-diazo-1,2-diphenylethanone (azibenzil, **33**) with phenyl thiophen-2-yl thioketone (**34**) in toluene solution, after 2 min irradiation gave a mixture of 1,3-oxathiole **35** and thietan-2-one **36** (Scheme 7). This result demonstrates the intermediacy of the carbene formed via elimination of N_2 from **33**, which either reacts with thioketone **34** to give a thiocarbonyl ylide or, alternatively, undergoes the Wolff rearrangement to yield diphenylketene. The latter reacts in a regioselective [2+2]-cycloaddition with **34** forming **36**. The [2+2]-cycloaddition of diphenylketene with diverse hetarylthioketones, including **34**, has been reported recently [20].



Scheme 7. Microwave-assisted reaction of azibenzil (**33**) with phenyl thiophen-2-yl thioketone (**34**).

The formation of benzoyl phenyl ketene and its subsequent trapping with the cycloaliphatic thioketone **24** was also observed in the reaction of the latter with 2-diazo-1,3-diphenylpropane-1,3-dione (**37**) while heating at 80°C in toluene [21] (Scheme 8). Along with products **38** and **39**, resulting from the 1,5- and 1,3-dipolar electrocyclization reactions of the intermediate thiocarbonyl ylide, the six-membered product **40** is formed as the [4+2]-cycloadduct of the starting thioketone **24** with the in situ formed ketene.

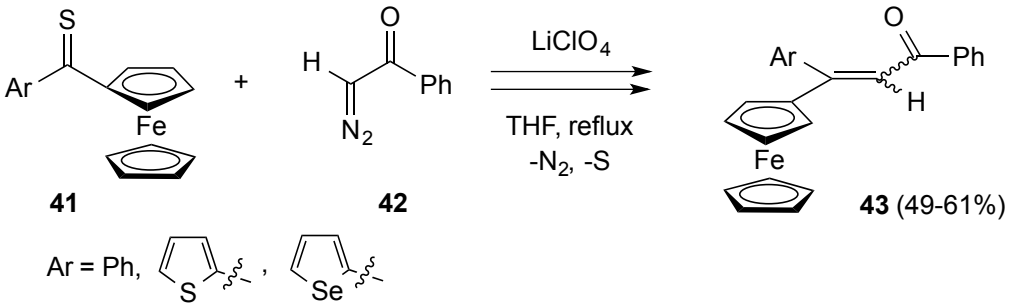


Scheme 8. Reaction of the in situ formed dibenzoylcarbene and benzoyl phenyl ketene, respectively, with thioketone **24**.

Similarly, thermal reactions of thiobenzophenone (**25**) with differently substituted 2-diazocyclohexane-1,3-diones occurred via a cascade of conversions initiated by the in situ formed diketocarbene. After Wolff rearrangement of the latter and hetero-Diels-Alder reaction of the α-oxoketene with **25**, the corresponding 1,3-oxathiin-4-one is formed in up to 71% yield [22]. Dimerizations of the ketenes occurred also as [4+2]-cycloadditions. Finally, the initially formed carbenes combine with the C=S group of **25** forming diketo thiocarbonyl ylides, which subsequently undergo 1,5-dipolar electrocyclizations to give bicyclic 1,3-oxathioles.

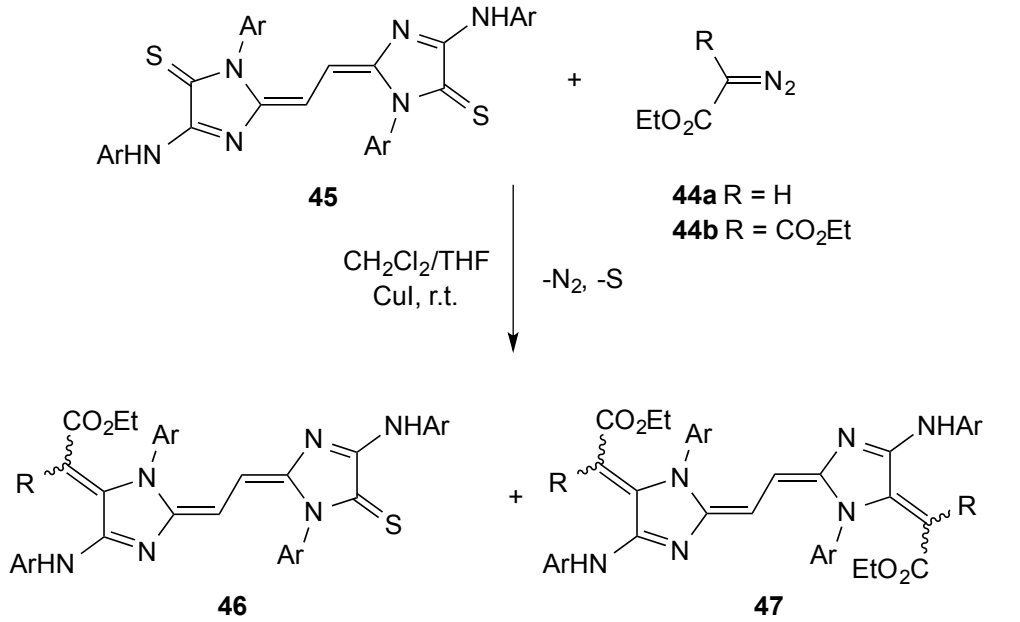
Ferrocenyl-substituted thioketones and their reaction with diazo compounds have extensively been studied [23]. The attempted reaction of ferrocenyl phenyl thioketone (**41**, Ar = Ph) with diazoacetophenone (**42**) performed in boiling THF in the presence of $LiClO_4$ led to the corresponding (*E*)- and (*Z*)-ethene derivatives

43 (Ar = Ph) in 49% yield [19] (Scheme 9). Similar results were obtained with ferrocenyl hetaryl thioketones bearing a thien-2-yl or selenophen-2-yl substituent. However, the microwave-assisted experiments with these thioketones resulted in their decomposition. On the other hand, the reactions of N-benzoyl diazoproline **29** (R^1 = PhCO) with **31** and its Se analogue performed under MW irradiation led to the corresponding ethenes **32** (Scheme 6) in high yields [19].



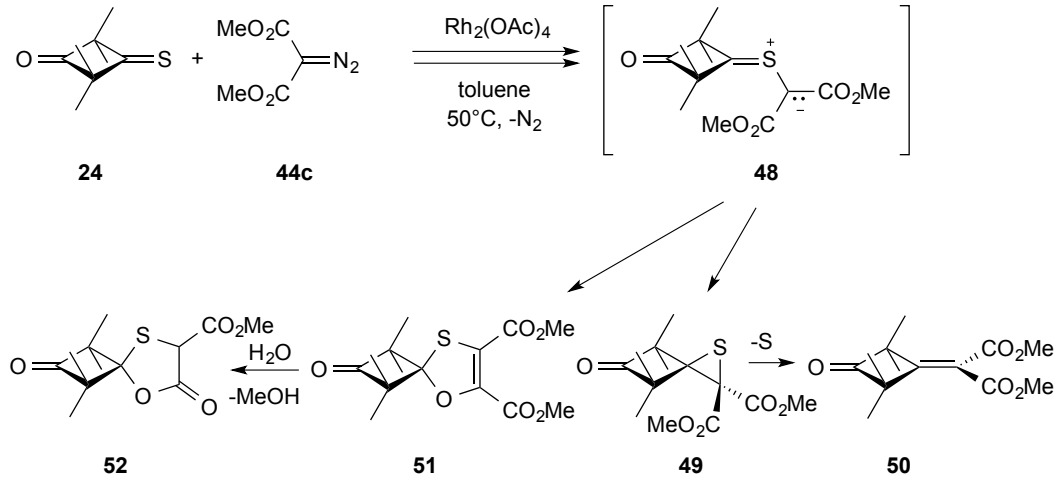
Scheme 9. Formation of β-ferrocenyl-α,β-unsaturated ketones **43** (chalcones).

The 'two-fold extrusion reaction' (Barton-Kellogg olefination) comprises sequential elimination of N_2 and S in reactions of thiocarbonyl compounds with diazomethanes as discussed in the previous sections. In the case of less reactive diazoesters **44**, this reaction requires metal catalysis to generate the reactive carbenoid. The conjugated bis thioxoimidazole system **45** was converted into the products **46** and **47** with most extended π-systems upon treatment with ethyl diazoacetate or diethyl diazomalonate [24] (Scheme 10). In these reactions, decomposition of the diazo-compound was induced by CuI or by the $PdCl_2(PPh_3)_2$ complex, and elimination of sulfur occurred spontaneously.



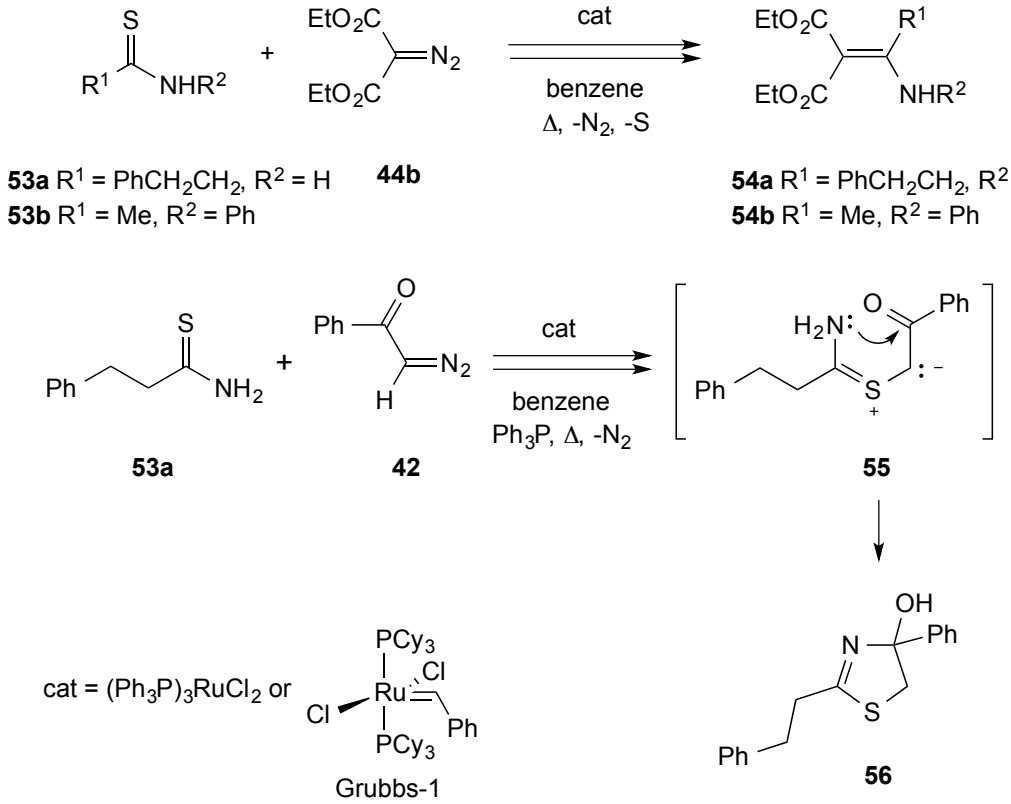
Scheme 10. Copper(I)-catalyzed decomposition of α-diazoesters **44** in the presence of bis(4-thioxoimidazoles) **45**.

The cycloaliphatic thioketone **24** reacted with dimethyl diazomalonate (**44c**) in the presence of $Rh_2(OAc)_4$ in toluene at 50°C. In that case, along with the olefinic product **50**, 1,3-oxathiolan-5-one **52** was obtained after hydrolysis of the intermediate acetal **51**, which results from the 1,5-dipolar electrocyclization of the thiocarbonyl ylide **48** [25] (Scheme 11).



Scheme 11. Competitive 1,3- and 1,5-dipolar electrocyclizations of the transient thiocarbonyl ylide **48**.

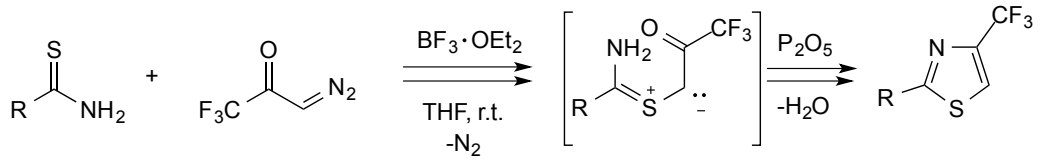
Thioamides are known as poor dipolarophiles, and for that reason, their reactions with diazoesters and diazoketones occur only via metal assisted generation of a corresponding carbene. Primary and secondary thioamides were converted into the corresponding enaminones or enaminoesters **54** by Ru-catalyzed reactions with diethyl diazomalonate (**44b**), ethyl 2-diazoacetylacetate (**44d**), or 2-diazodimedone (**20**) [26,27]. The formation of the enaminones resulted from the known 'two-fold extrusion pathway' with an intermediate amino-functionalized thiocarbonyl ylide (Scheme 12). However, in the case of diazoacetophenone (**42**) and 3-phenylpropanethioamide (**53a**), the intermediate thiocarbonyl ylide **55** underwent a new 1,5-heterocyclization leading to 1,3-thiazole derivative **56** and the expected enaminone was not formed.



Scheme 12. Formation of enaminoesters **54** (above) and 4,5-dihydro-1,3-thiazole **56** (below) in the reactions of thioamides **53** with diazo compounds **44b** and **42**, respectively.

Alternatively to this interpretation of the reaction mechanism via an intermediate thiocarbonyl ylide, the insertion reaction of the carbenoid into the S–H bond of the tautomeric form of the thioamide can also be considered.

A cyclization of an amino-functionalized thiocarbonyl ylide analogous to **55** was recently reported for the BF_3•OEt_2-catalyzed reactions of thiobenzamides and thiourea, respectively, with diazo(trifluoro)acetone (**57**) [28] (Scheme 13). In this reaction, BF_3•OEt_2, added as a catalyst, induced the formation of a carbene-like species, which react to give thiocarbonyl ylides of type **58**, and in addition promotes the formation of the 1,3-thiazoles **59** and not the 1,5-dipolar electrocyclization leading to the 1,3-oxathioles.



53c R = Ph
53d R = NH_2

57

58

59a R = Ph (52%)
59b R = NH_2 (62%)

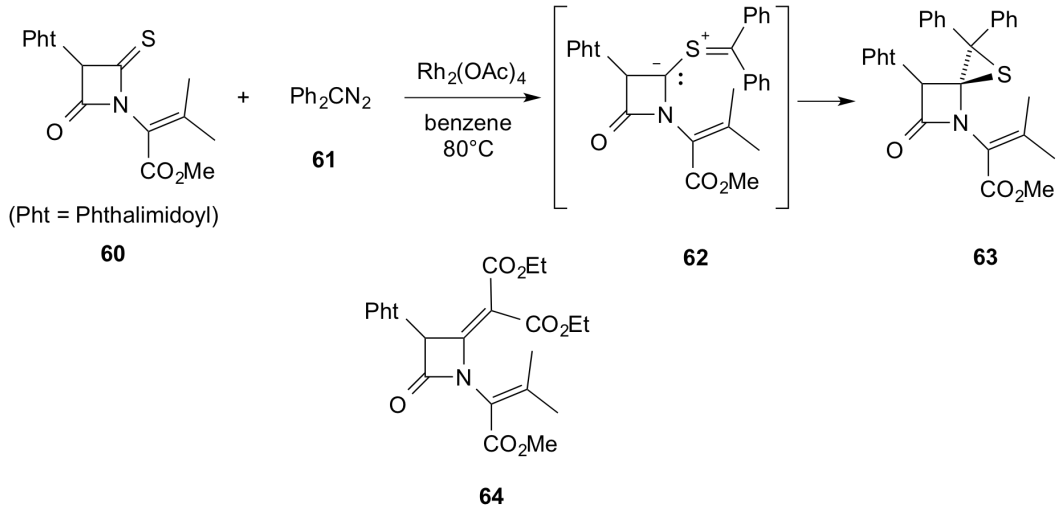
Scheme 13. Formation of 4-trifluoromethyl-1,3-thiazoles **59** from thioamides **53** via the reactive thiocarbonyl ylide **58**.

A series of 4-trifluoromethyl-1,3-thiazole-5-carboxylates was obtained starting with arylthioamides and ethyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate in the presence of a rhodium catalyst ($Rh_2(NHCOC_3F_7)_4$) in 1,2-dichloroethane in good yields (63–68%) [29]. The reaction was accelerated by microwave irradiation. The initially formed products, 4-hydroxy-4-trifluoromethyl-1,3-thiazoline-5-carboxylates, were dehydrated at room temperature by addition of DBU.

Aromatic thioamides undergo a Cu(I)-catalyzed reaction with diverse α-diazoacetylacetates in boiling toluene, and the expected 1,3-thiazole-5-carboxylates were obtained in 60–72% yield [30]. In contrast to the above described reactions leading to trifluoromethylated 4-hydroxy-1,3-thiazolines, elimination of H_2O resulting in the aromatization of the heterocycle occurs spontaneously under the reaction conditions. The authors explained the reaction pathway via the S–H insertion mechanism, but the formation of the corresponding thiocarbonyl ylide as reactive intermediate is also a likely interpretation.

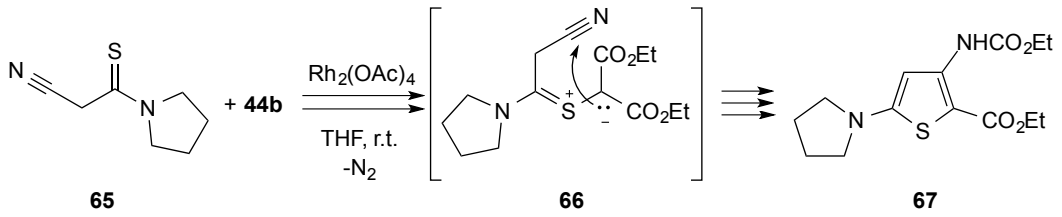
In the case of non-enolizable thioamides, e.g. 4-thioxoazetidin-2-one **60**, the $Rh_2(OAc)_4$-mediated reaction with diphenyldiazomethane (**61**) occurred via the in situ generated carbenoid, which after electrophilic attack on the C=S group

formed the intermediate thiocarbonyl ylide **62** [31] (Scheme 14). After the subsequent 1,3-dipolar electrocyclization, thiirane **63** was obtained as the final product in 65% yield. The analogous reaction with ethyl diazomalonate (**44b**) required excess of the latter and a spontaneous desulfurization of the unstable thiirane led to alkylideneazetidinone **64**, isolated in 58% yield. Apparently, the intermediate carbenoid reacted faster with the thiirane then with the starting thiocarbonyl compounds **60**.



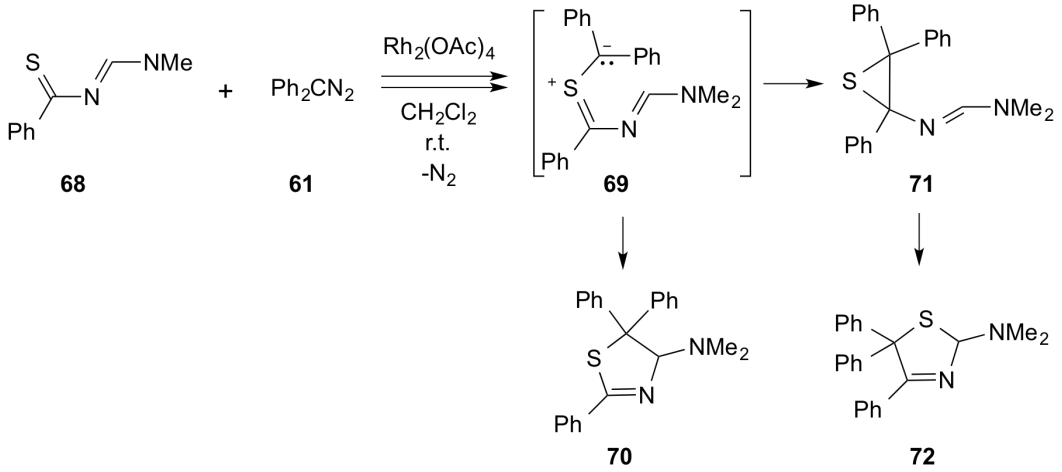
Scheme 14. Conversion of 4-thioxoazetidin-2-one **60** into thiirane derivatives **63** and alkylideneazetidinone **64** in Rh-mediated reactions with diazo compounds.

Thioamides of type **65** derived from cyanothioacetic acid react with the in situ generated carbenoid via N_2 elimination from diethyl diazomalonate, diazodimedone or ethyl diazocyanoacetate, and 3,5-diaminothiophene-2-carboxylates were obtained in high yields [32] (Scheme 15). For the decomposition of the diazo compounds, Rh(II)-carboxylates were used in catalytic amounts. As an example, the reaction of 3-(pyrrolidin-1-yl)-3-thioxopropanenitrile (**65**) with diethyl diazomalonate (**44b**) is depicted in Scheme 15. The highly functionalized thiocarbonyl ylide **66** undergoes a new heterocyclization via nucleophilic attack of the anionic terminus of the 1,3-dipole onto the cyano group to form the thiophene ring. After migration of one ester group onto the C=NH moiety, aromatization of the heterocyclic ring occurs to give **67**.



Scheme 15. Multi-step reaction leading to thiophene derivative **67** via thiocarbonyl ylide **66** derived from (α-cyanomethyl)thioamide **65**.

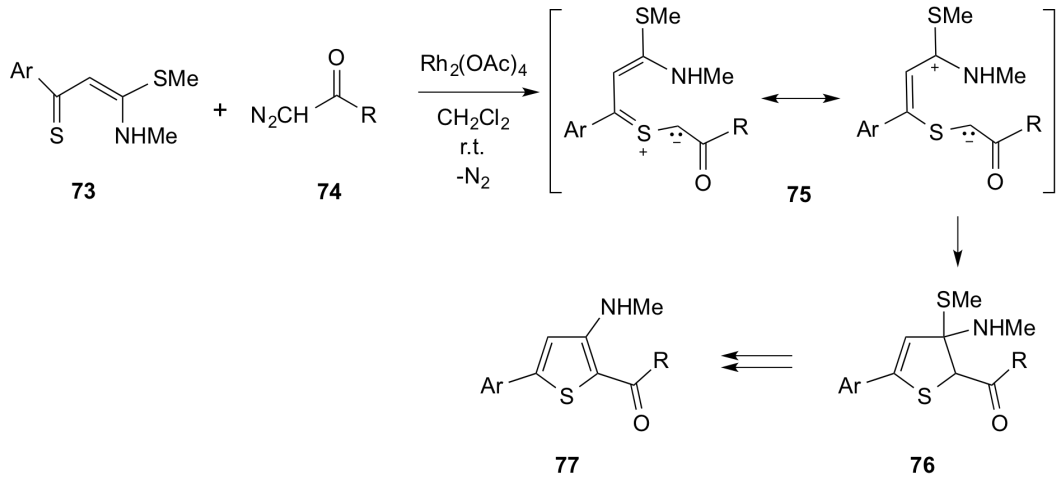
The thiobenzamide derivative **68** was used in the reaction with diphenyldiazomethane (**61**) in the presence of $Rh_2(OAc)_4$ yielding two isomeric dihydro-1,3-thiazoles **70** and **72** via an intermediate thiocarbonyl ylide **69** [33] (Scheme 16). Whereas product **70** results from 1,5-dipolar electrocyclization of **69**, the formation of **72** was explained via initial 1,3-dipolar electrocyclization to give thiirane **71**, which subsequently undergoes a ring-opening/ring-closure sequence.



Scheme 16. Competitive formations of 1,3-thiazolines **70** and **72** via dipolar electrocyclization reactions of the intermediate α-imino-substituted thiocarbonyl ylide **69.**

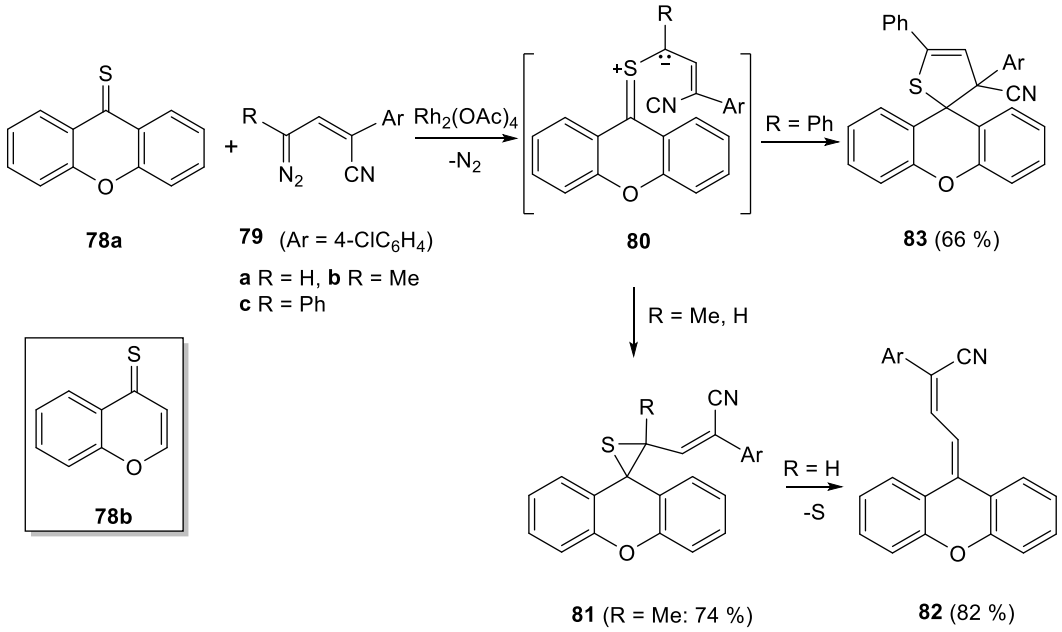
The α,β-unsaturated thioketones (thiobenzoylketene *S*,*N*-acetals) **73** react with Rh-carbenoids generated from α-diazoketones and esters of type **74** to give substituted thiocarbonyl ylides **75** as intermediates [34] (Scheme 17). Subsequent chemoselective 1,5-dipolar electrocyclization yields 2,3-dihydrothiophenes **76**,

which undergo further transformations to give 2-acylthiophenes **77** as the major products in 53–67% yield.



Scheme 17. Synthesis of 2-acyl-3-aminothiophenes **77** from thiobenzoylketene *S*,*N*-acetals **73** via an intermediate thiocarbonyl ylide **75**.

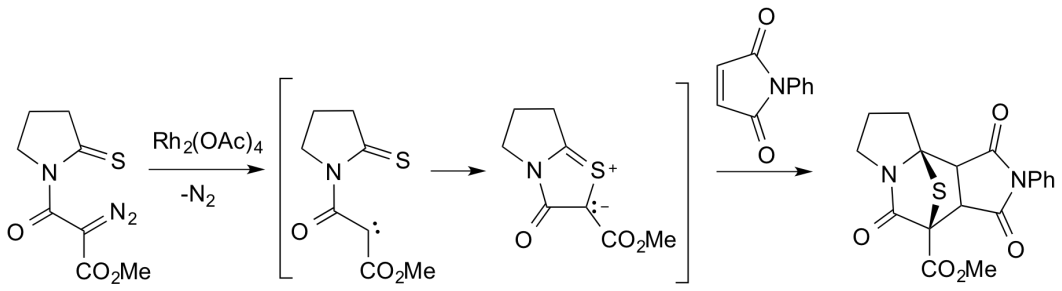
A similar sequence with a α-vinyl-substituted thiocarbonyl ylide as an intermediate was proposed for the reaction of the aromatic thioketones **78** with α-vinyl diazomethanes **79** [35] (Scheme 18). The elusive thiocarbonyl ylides **80** formed in the presence of $Rh_2(OAc)_4$ underwent either 1,3- or 1,5-dipolar electrocyclization depending on the type of substituent R of the diazo compound. Whereas reactions of xanthione (**78a**) with **79a**,**b** led to thiiranes **81**, the product formed with **79c** was identified as spirocyclic dihydrothiophene **83**. In the case of **81** (R = H), the unstable thiirane extruded spontaneously sulfur to give the corresponding diene **82**. Analogous results were obtained with thiochromone (**78b**).



Scheme 18. Rhodium-catalyzed reactions of α-vinyl diazomethanes **79** with 9*H*-xanthene-9-thione (**78a**).

2.2. Intramolecular reactions

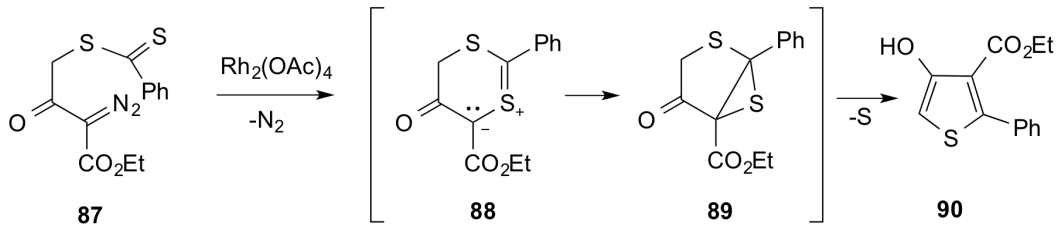
The intramolecular reactions of diazo compounds containing a thiocarbonyl moiety offer a convenient access to cyclic or polycyclic products with preservation or extrusion of the sulfur atom. In a pioneering work, Padwa described a protocol for the intramolecular formation of reactive thiocarbonyl ylides, which were efficiently trapped with common dipolarophiles such as *N*-phenylmaleimide or dimethyl acetylenedicarboxylate [36]. A representative example with diazo compound **84** and the polycyclic product **86** is depicted in Scheme 19. The intermediate thiocarbonyl ylide **85** was postulated as 1,3-dipole, which enter the [3+2]-cycloaddition with *N*-phenylmaleimide to give **86** in 75% yield. The intermediate thiocarbonyl ylide **85** is stabilized as a mesoionic system and reacts easily with the added dipolarophile.



84 **85** **86**

Scheme 19. Trapping of the intermediate thiocarbonyl ylide **85** with *N*-phenylmaleimide.

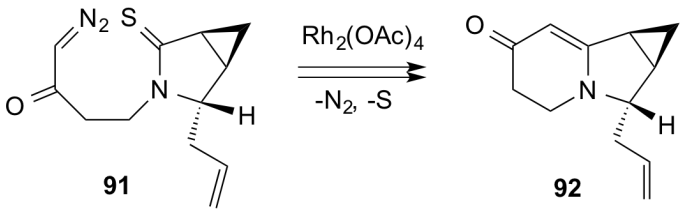
However, in a similar six-membered system **88**, generated from diazo dithioester **87**, the 1,3-dipolar electrocyclization is the fastest reaction leading to the unstable bicyclic thiirane **89**, which extrudes sulfur to give thiophene **90** in 80% yield [37] (Scheme 20). In the same publication, similar reactions with intramolecularly formed thiocarbonyl ylides, which undergo either 1,3-dipolar electrocyclization or react with a suitable dipolarophile, are described.



87 **88** **89** **90**

Scheme 20. The formation of an instable thiirane **89** from thiocarbonyl ylide **88** and its spontaneous desulfurization.

The same concept was applied successfully by Danishefski in the multistep synthesis of indolizomycin [38,39]. Starting with diazothioamide **91**, the $Rh_2(OAc)_4$-catalyzed decomposition led to the expected product **92** via a tricyclic thiocarbonyl ylide and an unstable thiirane formed therefrom, and its subsequent desulfurization (Scheme 21).

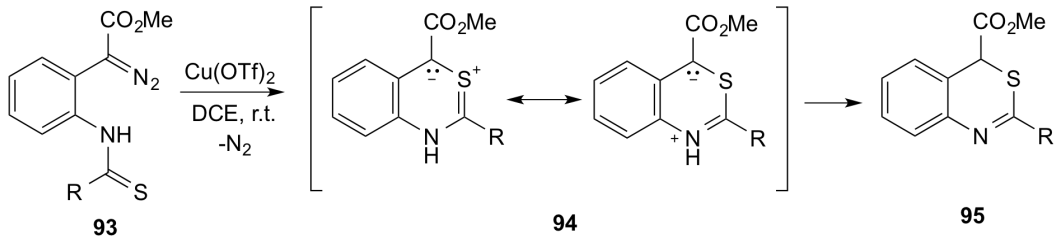


Scheme 21. Intramolecular formation of a thiocarbonyl ylide (not shown) and elimination of sulfur from an intermediate thiirane leading to the indolizomycin skeleton **92**.

In the same study, an intermolecular version of this reaction sequence, starting with ethyl diazoacetate (**44a**) and a tricyclic thioamide, was also reported for the synthesis of a methylene analogue of **92**.

The method applied for the preparation of indolizomycin with an intramolecular generation of the thiocarbonyl ylide and desulfurization of the isomeric stable thiirane by treatment with Raney-Ni was also explored for the synthesis of an analogue of an ACE inhibitor [40].

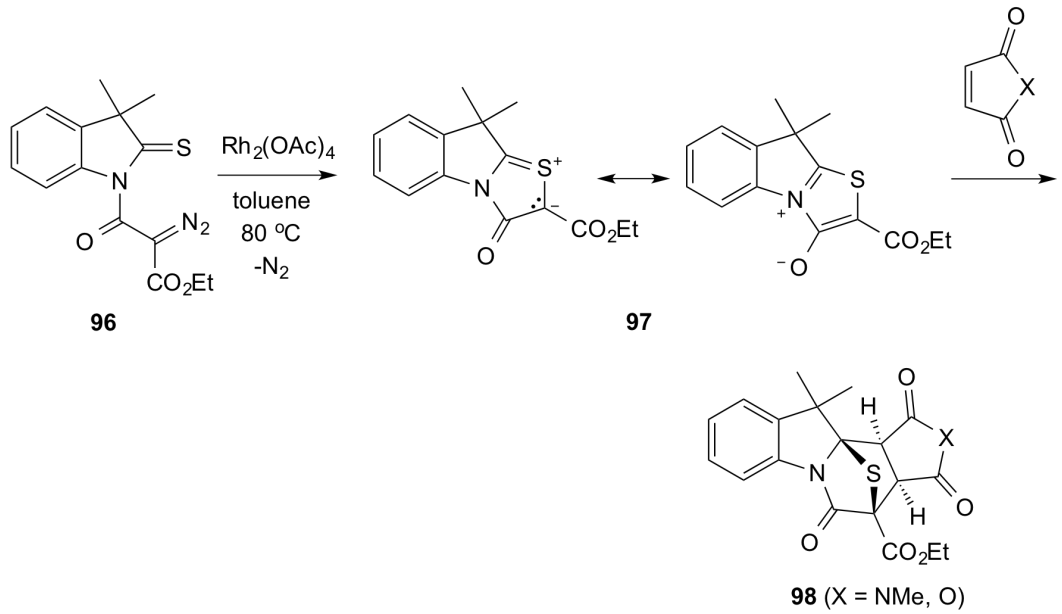
Another series of aromatic thioamides of type **93** was applied as starting materials for the synthesis of 4*H*-benzo[*d*][1,3]thiazines **95** via $Cu(OTf)_2$-catalyzed decomposition in 1,2-dichloroethane at room temperature [41] (Scheme 22). The reported yields of products were in the range of 75–80%. The initially formed thiocarbonyl ylides **94** undergo a proton migration yielding the final products **95**.



Scheme 22. Stabilization of the intermediate thiocarbonyl ylides **94** via proton migration.

The decomposition of the indole-based diazothioamide **96** in toluene using $Rh_2(OAc)_4$ as a catalyst leads to the expected thiocarbonyl ylide/thioisomünchnone **97** as a stable product [42] (Scheme 23). The structure of this crystalline compound was confirmed by X-ray single crystal analysis. When

the decomposition of **96** was performed in the presence of *N*-methylmaleimide or maleic acid anhydride as dipolarophile, the polycyclic [3+2]-cycloadducts **98** were obtained in 66 and 65% yield, respectively.

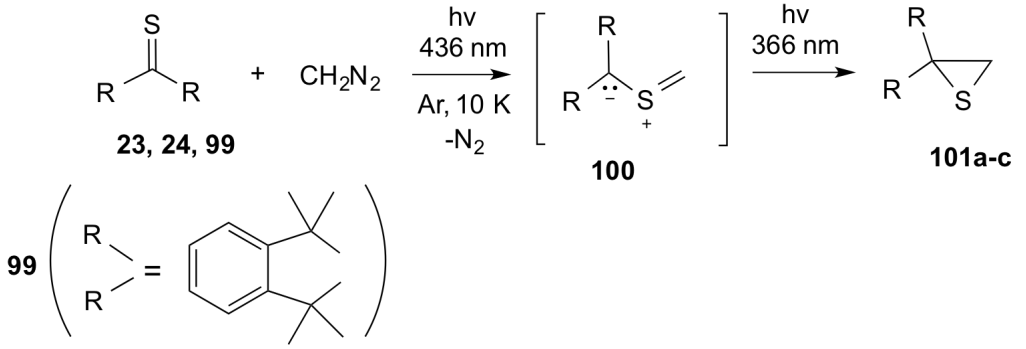


Scheme 23. Decomposition of **96** leading to the 1,3-dipolar species **97** and its [3+2]-cycloaddition reaction.

3. Reactions of free carbenes with thiocarbonyl compounds

3.1. Reactions with electrophilic carbenes

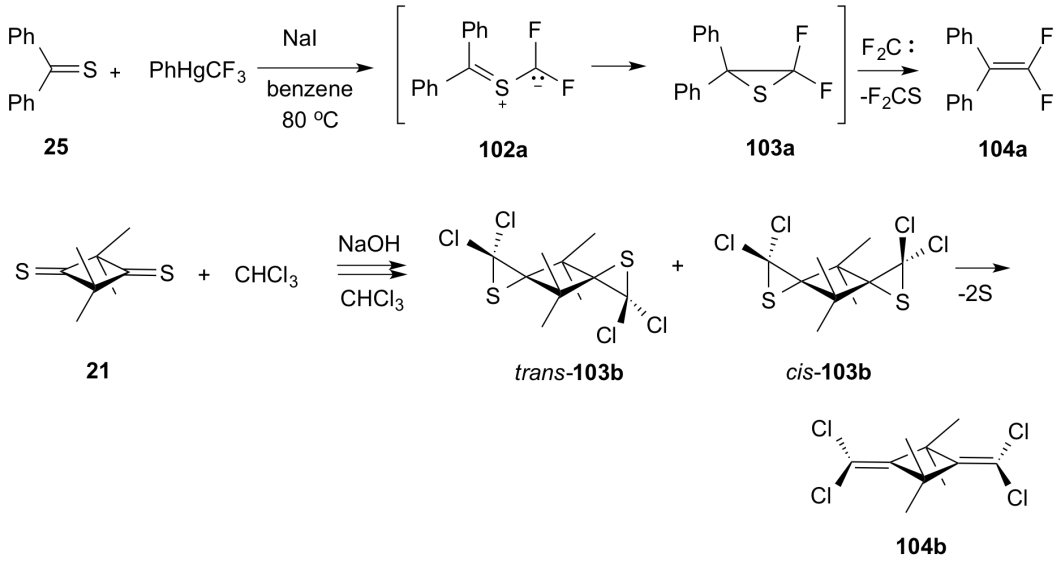
Thiocarbonyl ylides of type **100** were generated in Argon matrices at 10 K or in an organic glass at 77 K by photodecomposition of diazomethane in the presence of thioketones **23**, **24**, and **99** [43] (Scheme 24). Whereas the decomposition of diazomethane was achieved by using UV light with $\lambda = 436$ nm, the subsequent cyclization to thiiranes **101** was performed by irradiation with using wavelength $\lambda = 366$ nm. The identification of the intermediates **100** and final products **101** was based on UV spectra. In agreement with theoretical calculations, thiocarbonyl ylides **100** showed a distinct absorption at $\lambda = 350$ nm.



Scheme 24. Photochemical generation of thiocarbonyl methanides **100** in Ar matrix.

A similar study with tetrasubstituted thiocarbonyl ylides derived from aromatic diazo compounds and aliphatic thioketones has also been reported [44].

Dihalocarbenes, generated thermally from Seyferth reagent ($PhHgCF_3$) or in a two-phase system from $CHCl_3$, react smoothly with aromatic and cycloaliphatic thioketones yielding 2,2-dihalothiiranes **103** as initial products, which in some cases underwent desulfurization to give the corresponding gem-dihaloethylene derivatives **104**. Two representative examples of these reactions with thiobenzophenone (**25**) and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**21**) are presented in Scheme 25 [45,46]. The mechanistic explanation is based on the assumption that dihalo-substituted thiocarbonyl ylides **102** are the key intermediates and the excess of dihalocarbene acts as desulfurating agent. Nevertheless, competitive, asynchronous [2+1]-cycloadditions of highly electrophilic dihalocarbenes onto the C=S double bond cannot be excluded. It should be emphasized that in these reactions secondary products observed in the case of thiocarbonyl ylides (1,3-dithiolanes, 1,4-dithianes) playing the role of reactive intermediates, have never been reported.



Scheme 25. Reactions of dihalocarbenes with an aromatic and a cycloaliphatic thioketone.

The stability of the gem-dihalothiiranes depends on the substitution pattern. Thus, thiirane **103a** undergoes spontaneous desulfurization, but the sterically crowded bisspirothiiranes **103b** could be isolated after short reaction time.

A study on the reactions of sterically crowded bornane-2-thiones of type **105** with dichloro- and dibromocarbene generated from different precursors was reported recently [47]. Depending on the reaction conditions, the 2-methylidene derivative **106** or thioketene **107** and its dimer were isolated from the reaction mixture (Figure 1). Whereas products **106** are formed after spontaneous elimination of sulfur from the initial thiiranes, thioketenes **107** are proposed being formed via dehalogenation of the latter and rearrangement of the reactive thiiran-2-ylidene.

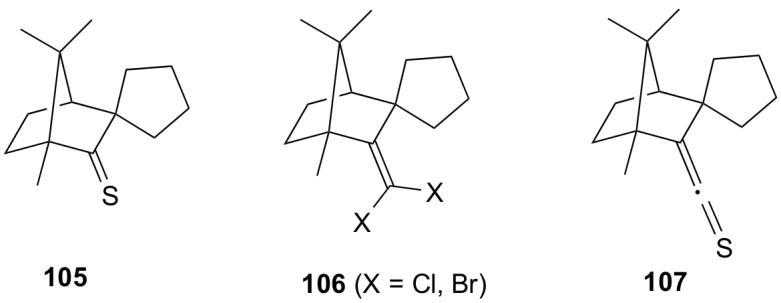
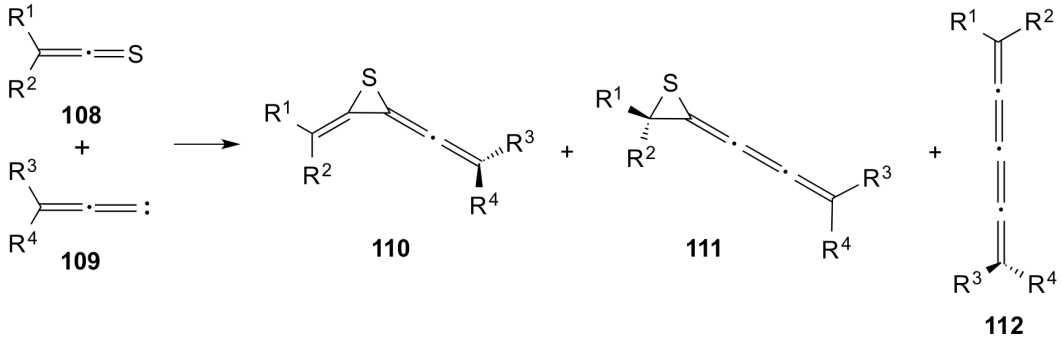


Figure 1. Products obtained from the reaction of **105** and dihalocarbenes via multistep mechanisms.

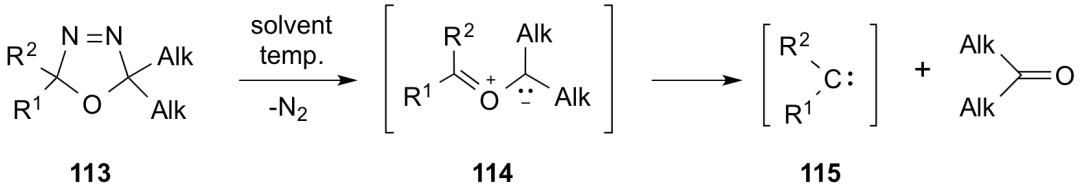
Sterically crowded thioketenes **108** (e.g. R^1 = R^2 = *tert*-butyl) react with alkylidene carbenes **109** (e.g. R^3 = R^4 = *tert*-butyl), generated from the corresponding haloallenes under phase-transfer conditions ($NaOH_{aq}$/benzene). Under these conditions, allenyl-vinyl-substituted thiiranes of type **110** were obtained as major products along with pentatetraenes **112** formed after desulfurization of thiiranes **110** [48] (Scheme 26). In one of the described cases, the isomeric trienylthiirane of type **111** was the major product. Its formation was explained as the result of the sulfur migration in the initially formed thiirane **110**. This problem was studied and reported in a further publication of the same group [49].



Scheme 26. Cumulene-substituted isomeric thiiranes **110**/**111** and the pentatetraene **112** resulting from their desulfurization.

3.2. Reactions with nucleophilic carbenes

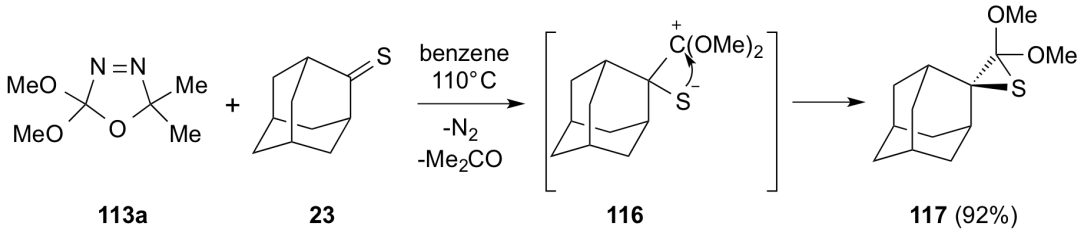
Relatively stable and isolable 2,5-dihydro-1,3,4-oxadiazoles (Δ^3-1,3,4-oxadiazolines) **113** are considered as convenient precursors of nucleophilic carbenes **115** bearing alkoxy (R^1 and/or R^2 = OAlk), alkylthio (R^1 and/or R^2 = SAlk) or alkylamino (R^1 and/or R^2 = NHAlk) groups (Scheme 27) [50].



Scheme 27. Thermal generation of nucleophilic carbenes **115**.

Mechanistic studies confirmed the intermediacy of carbonyl ylides **114**, which under thermal conditions in solution or in gas phase undergo decomposition and yield the corresponding carbene **115** side by side with the released carbonyl compound (i.e. ketone). Among nucleophilic carbenes of this type, the best known and synthetically widely explored one is dimethoxycarbene [$(MeO)_2C$:] (DMC, **115a**), which in the ground state appears as a singlet species that was demonstrated by gas-phase studies (FVP) [51].

Thermal decomposition of 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole (**113a**) can be easily achieved by heating in benzene or toluene solution at 60–110°C, and the reactions are performed with the in situ generated DMC (**115a**; $R^1 = R^2 = MeO$). Under these conditions some thiocarbonyl compounds (thioketones, thioesters, dithioesters, thioamides) were reacted with **115a** yielding diverse products depending on the type of starting thiocarbonyl substrates. Thus, a clean and efficient reaction with adamantanethione (**23**) leading to the first isolated 2,2-dimethoxythiirane **117** was successfully performed in benzene solution at 100°C (sealed tube) [52] (Scheme 28). Very likely, nucleophilic attack of **115a** onto the C=S bond results in the formation of the zwitterionic intermediate **116**, which in the next step undergoes the ring closure to give the three-membered ring of the stable spiro-thiirane **117**.

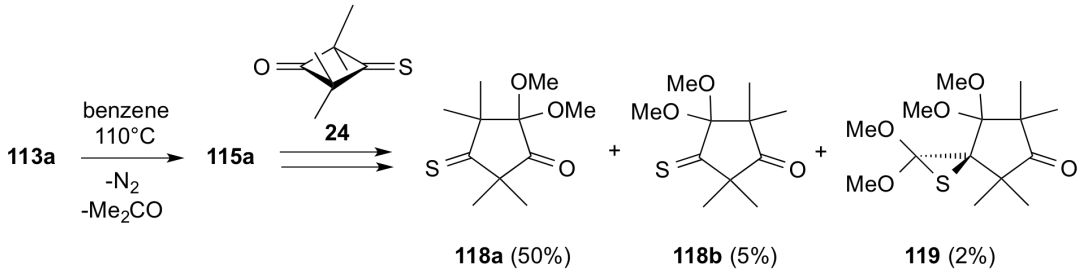


113a **23** **116** **117** (92%)

Scheme 28. The first dimethoxythiirane **117** derived from adamantanethione (**23**).

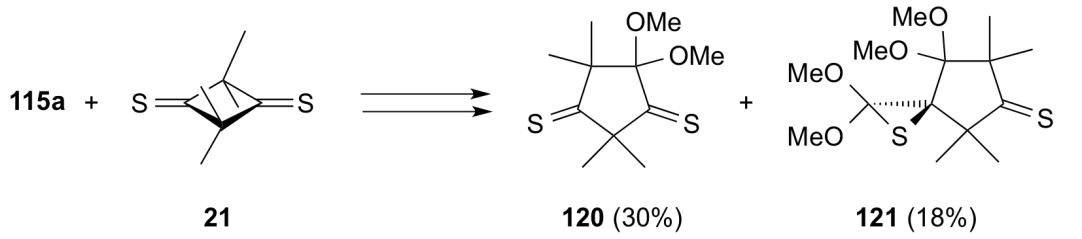
Under analogous conditions, reaction of the sterically crowded monothione **24** (3-thioxo-2,2,4,4-tetramethylcyclobutanone) occurred with initial ring expansion of the sterically congested cyclobutanone ring. Remarkably, this step of the reaction occurred regioselectively via addition of carbene **115a** on the C=O group and led to the formation of the five-membered monothione **118a** as the major product. The latter could be isolated from the reaction mixture side by side

with the isomeric monothione **118b**, formed via carbene addition on the C=S group, as the minor component (Scheme 29) [53]. The expected spiro-thiirane derived from **24** was not observed and only traces of the ring-expanded spiro-thiirane **119** were separated chromatographically from the crude mixture.



Scheme 29. Ring enlargement of 3-thioxo-2,2,4,4-tetramethylcyclobutanone (**24**) in the reaction with DMC (**115a).**

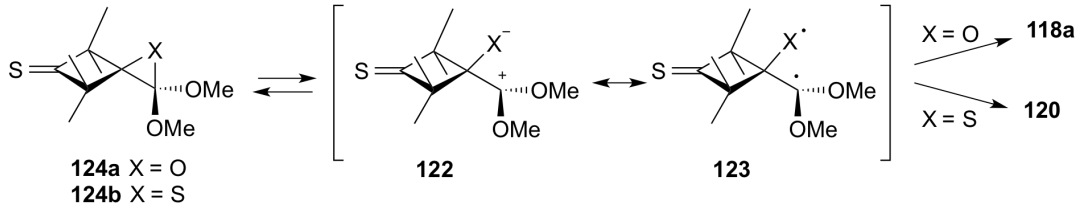
In the same publication, the reaction of DMC (**115a**) with dithione **21** (2,2,4,4-tetramethylcyclobutane-1,3-dithione) was also described, and in this system the ring expanded dithione **120** along with spiro-thiirane **121** were formed as two major components of the reaction mixture [53] (Scheme 30). Without doubt, the spiro-thiirane **121** is formed as a secondary product of the conversion from the initially produced cyclopentane-1,3-dithione **120**.



Scheme 30. Ring enlargement and thiirane formation in the reaction of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**21**) with DMC (**115a).**

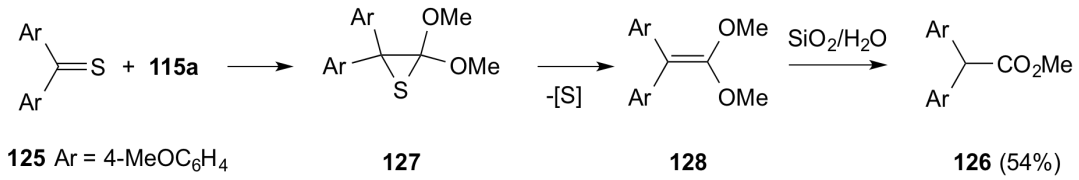
A plausible interpretation of the mechanism leading to the ring expanded products **118** and **120** is the intermediacy of zwitterionic (or diradical) species **122** and/or **123**, respectively, formed after nucleophilic attack of DMC onto the C=O or C=S group of the starting thioketones **24** or **21** (Scheme 31). An equilibrium of intermediates **122** and **123** with the corresponding spiro-oxirane **124a** (X = O) or

spiro-thiirane **124b** (X = S), respectively, was postulated to understand the observed reaction course [53].



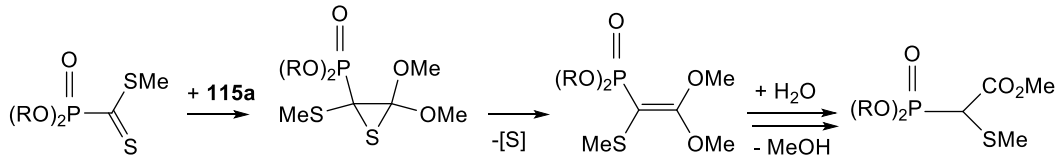
Scheme 31. Postulated mechanism of the ring enlargement step in the reactions of thioketones **21** and **24** with DMC (**115a**) with intermediacy of congested *spiro*-oxirane **124a** and *spiro*-thiirane **124b**, respectively.

Diaryl thioketone **125** (4,4'-dimethoxythiobenzophenone) was reported to react with DMC yielding, after a multi-step conversion, methyl diarylacetate **126** as the final product [54] (Scheme 32). The interpretation of the reaction mechanism is based on the assumption that after initial [1+2]-cycloaddition of DMC onto the C=S bond, leading to the labile thiirane **127**, spontaneous elimination of sulfur leads to ketene acetal **128**. This product undergoes hydrolysis upon chromatographic workup to give the ester **126** as the finally isolated product.



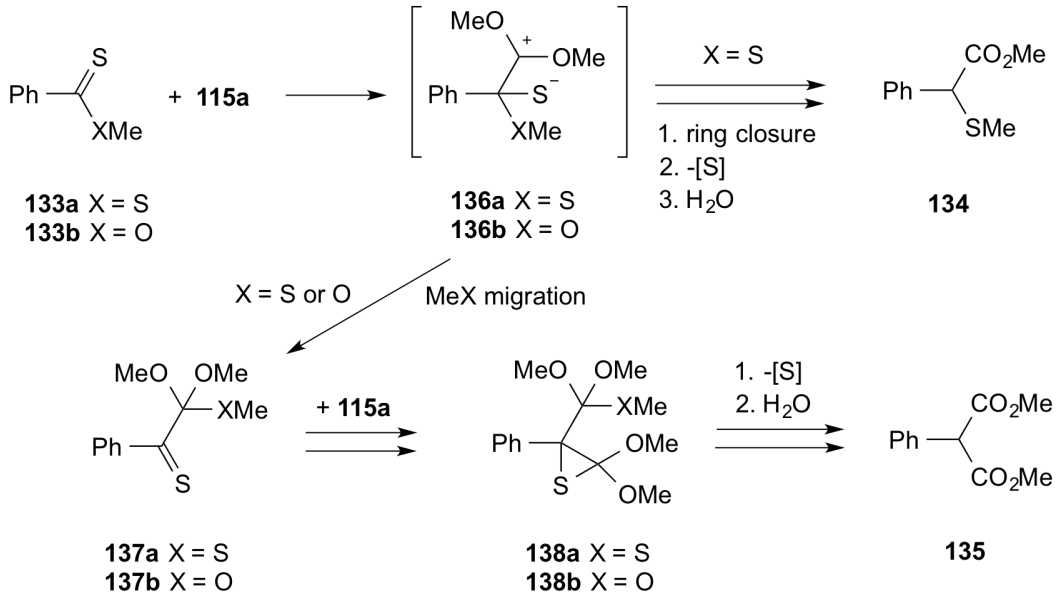
Scheme 32. Multi-step conversion of 4,4'-dimethoxythiobenzophenone (**125**) into methyl carboxylate **126**.

An analogous reaction sequence was proposed for the reaction of DMC with the phosphonylated dithioformate **129**, which in this multi-step reaction was converted into α-methylthio phosphonylethanoate **130** (50% yield). Consequently, also in this conversion, thiirane **131** and ketene acetal **132**, formed as a product of its desulfurization, are postulated as key intermediates [55] (Scheme 33).



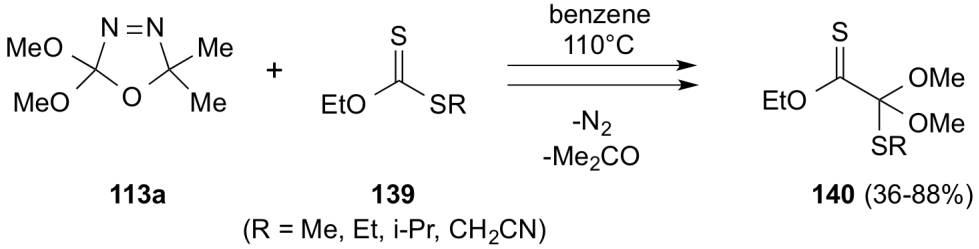
Scheme 33. Multi-step conversion of the phosphonylated dithioformate **129** into the α-methylthio phosphonylethanoate **130**.

Methyl dithiobenzoate (**133a**) reacts with DMC yielding two different products, i.e., a mixture of the expected 2-methylthio-2-phenylacetate **134** (22% yield) and dimethyl phenylmalonate (**135**) (28%). On the other hand, the reaction of DMC with methyl monothiobenzoate (**133b**) led to the ester **135** exclusively, obtained in 84% yield [54] (Scheme 34). These different reaction pathways were explained by an easy migration of the MeS and MeO group, respectively, in the intermediates **136** to give thioketones **137**, addition of a second carbene **115a** yielding thiiranes **138**, elimination of sulfur, and subsequent hydrolysis of the labile orthoester formed thereby. In the case of **136a**, competitive ring closure leads to the corresponding thiirane, followed by elimination of sulfur and hydrolysis. The intermediate **138b**, formed in the reaction with monothiobenzoate **133b**, could be detected by NMR spectroscopy.



Scheme 34. Multi-step reaction of methyl dithiobenzoate (**133a**) or methyl monothiobenzoate (**133b**) with DMC (**115a**) yielding 2-methylthio-2-phenylacetate **134** and/or dimethyl phenylmalonate (**135**).

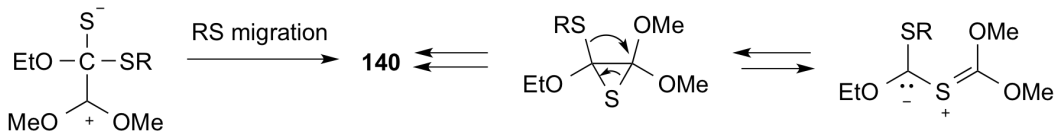
Xanthates **139** were also tested in thermal reactions with DMC (**115a**) performed in benzene solution at 110°C and in most cases afforded products of type **140** formed via insertion of DMC into the C–S single bond (yields varied from 36 to 88%) [56] (Scheme 35).



113a **139** (R = Me, Et, i-Pr, CH_2CN) **140** (36-88%)

Scheme 35. Insertion of DMC (**115a**) into the C–S bond in xanthates **139**.

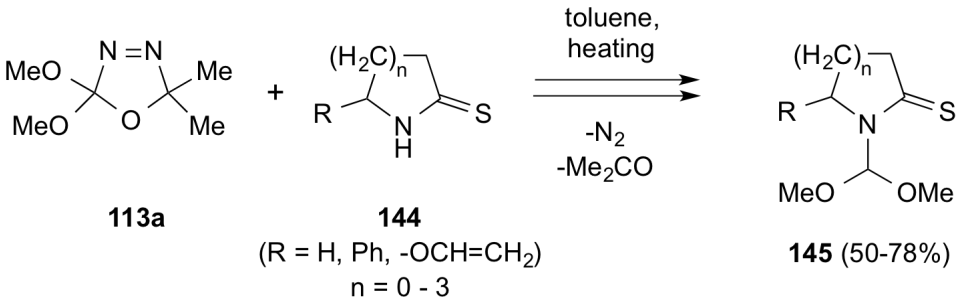
In this system, zwitterionic intermediates **141** are assumed to play a key role. However, participation of the alternative thiocarbonyl ylide **142** with subsequent ring closure leading to thiirane **143**, ring opening of the latter along the C–S bond and RS-migration, was also discussed [56] (Scheme 36).



141 **143** **142**

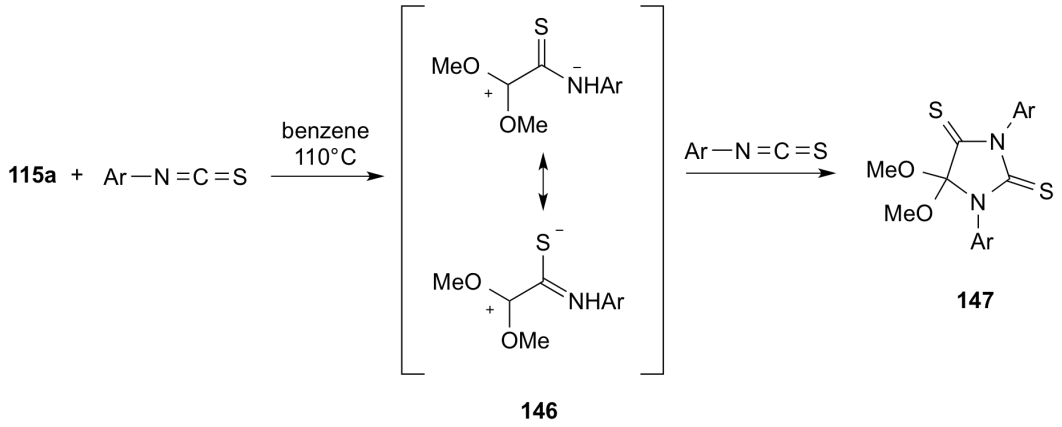
Scheme 36. Reaction mechanism of the RS group migration leading to thioacetate derivatives **140**.

Thermal generation of DMC in boiling toluene in the presence of equimolar amounts of a thiolactam **144** led exclusively to carbene insertion into the N–H bond and N-(dimethoxy)methyl derivatives of type **145** were obtained in these reactions in good yields (50–78%) [57] (Scheme 37).



Scheme 37. Chemoselective insertion of DMC (**115a**) into the N–H bond of thiolactams **144**.

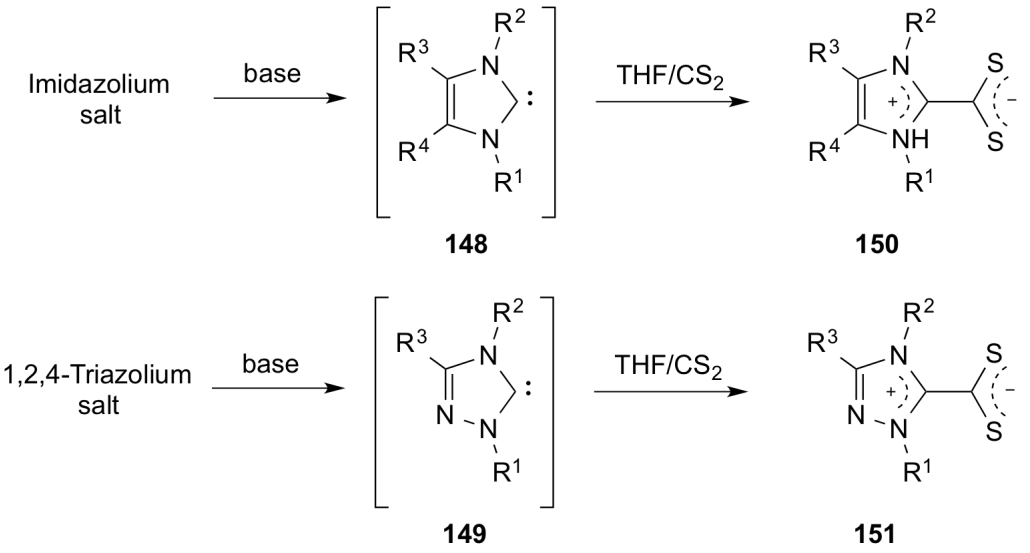
Reactions of DMC (**115a**) with aryl isothiocyanates occur in a different manner and deserve attention as they lead to new heterocyclic products. In these reactions, attack of the nucleophilic carbene onto the heterocumulene –N=C=S unit leads to the short-lived dipolar intermediate **146**, which subsequently is efficiently trapped by another molecule of the starting aryl isothiocyanate yielding the five-membered imidazolidine-2,5-dithione **147** as the product of a regioselective [3+2]-cycloaddition [58] (Scheme 38).



Scheme 38. Trapping of intermediate 1,3-dipolar species **146** generated in the reaction of aryl isothiocyanates with DMC (**115a**).

Since the discovery of the first, stable nucleophilic carbenes derived from bulky substituted imidazoles, i.e. imidazol-2-ylidenes [59], this exceptional class of organic compounds, abbreviated currently as NHCs (Nucleophilic Heterocyclic Carbenes), changed from ‘laboratory curiosities’ to important tools with crucial importance for versatile applications in organic synthesis, including asymmetric synthesis, and production of new materials [60,61]. In fact, reactions of NHCs

with thiocarbonyl compounds are lesser known, except the reactions with carbon disulfide (CS_2) and aryl isothiocyanates (Ar−N=C=S), which are of great importance. Hetaryl-2-ylidenes **148** and **149** react efficiently with CS_2 and form surprisingly stable zwitterionic hetarylium dithiocarboxylates, which in many instances were isolated and characterized by means of analytical and spectroscopic methods [62]. Selected general structures for imidazol-2-ylidene and 1,2,4-triazol-5-ylidene derivatives **150** and **151**, respectively, are depicted in Scheme 39. Their formation and physicochemical properties are reported in numerous publications and their great utility for the synthesis of diverse metal complexes with ruthenium, palladium, molybdenium and other transition metals has widely been explored. These aspects of the chemistry of zwitterionic dithiocarboxylates are summarized in two excellent reviews [63,64].

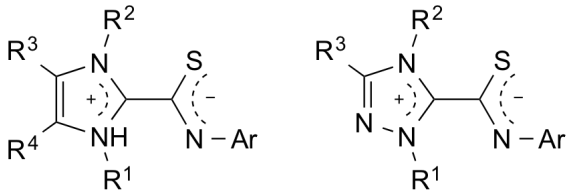


148 150

149 151

Scheme 39. Trapping of nucleophilic carbenes with carbon disulfide leading to zwitterionic hetarylium dithiocarboxylates **150** and **151** derived from imidazole and 1,2,4-triazole, respectively.

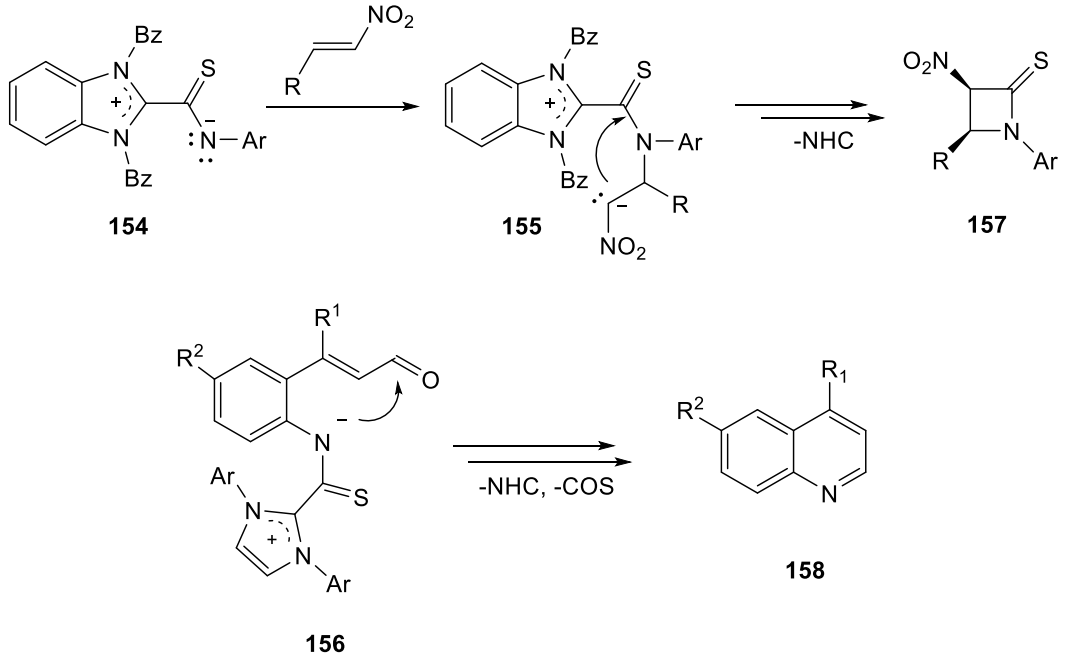
Structurally similar but less stable zwitterionic adducts (betaines) **152** and **153** are formed in reactions of NHCs with aryl isothiocyanates, and some of them are also of practical importance [63] (Figure 2).



152 **153**

Figure 2. Zwitterionic hetarylium imidothioates **152** and **153** obtained in reactions of isothiocyanates with nucleophilic carbenes derived from imidazole and 1,2,4-triazole, respectively.

For example, zwitterionic species **154**, **155**, and **156** were postulated as key intermediates in the NHC-catalyzed inter- and intramolecular conversions of corresponding isothiocyanates into β-thiolactams **157** [65] and quinoline derivatives **158** [66], respectively (Scheme 40). In the latter report, an alternative multi-step reaction initiated by the attack of NHC onto the aldehyde group, leading to indoline-2-thiones, without elimination of COS, is also described.



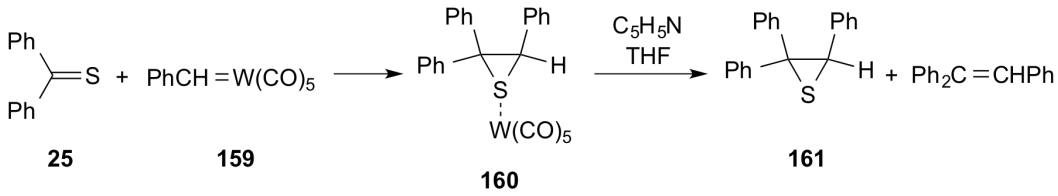
154 **155** **157**

156 **158**

Scheme 40. The NHC-catalyzed inter- and intramolecular transformations of some aryl isothiocyanates into β-thiolactams **157** and quinolines **158**, respectively.

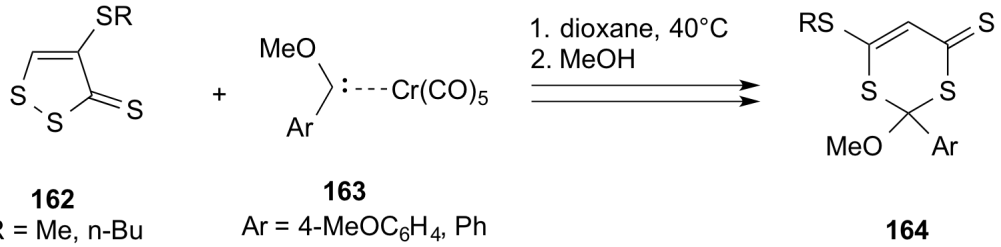
4. Reactions with stable metal-carbene complexes

Thiobenzophenone (**25**) was reported to undergo formal [2+1]-cycloaddition with (benzylidene)phenylmethylene applied as the tungsten Fischer complex **159**. The initially formed thiirane complex **160** was decomposed by addition of pyridine in THF solution. Finally, a mixture of 2,2,3-triphenylthiirane (**161**) and triphenylethylene being the product of its desulfurization was isolated from the reaction mixture [67] (Scheme 41).



Scheme 41. The [2+1]-cycloaddition of tungsten-complexed phenylmethylene (PhCH:) with thiobenzophenone (**25**).

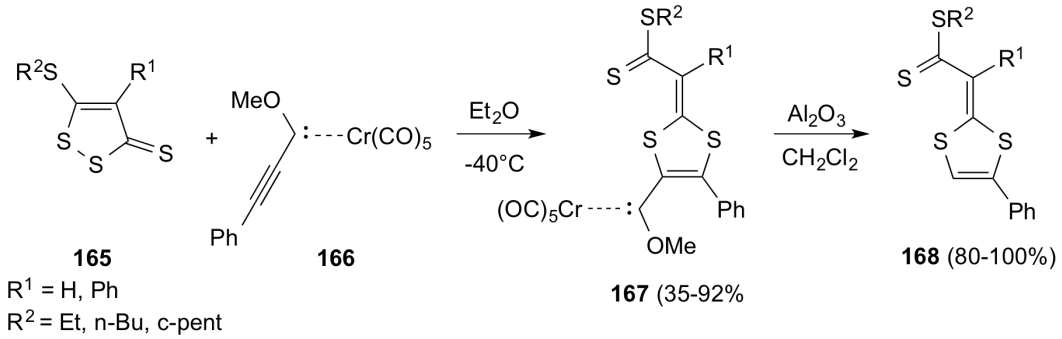
A different reaction course was observed in reactions of 1,2-dithiole-3-thiones **162** after treatment with chromium complexes **163**. In this system, no interaction of the carbene fragment with the C=S bond was observed, but instead ring enlargement via insertion of methoxybenzylidene into the S–S bond led to six-membered 4*H*-1,3-dithiin-4-thiones **164** [68,69] (Scheme 42).



Scheme 42. Ring enlargement of 1,2-dithiole-3-thiones **162** to 1,3-dithiin-4-thione derivatives **164** in reactions with chromium-complexed methoxybenzylidene (**163**).

Notably, a similar reaction of 1,2-dithiole-3-thiones **165** with the phenylethynyl Fischer chromium complex **166** yielded regioselectively the complexed dithiafulvene derivatives **167** as the product of a formal [3+2]-cycloaddition of the S(2)–C=S fragment of **165** with the triple C≡C bond located

in the carbene fragment acting as a dipolarophile [70] (Scheme 43). Decomplexation by treatment with Al_2O_3 in dichloromethane led to the dithiafulvenes **168**. Thus, in this case, the complexed nucleophilic carbene has not been involved in an interaction with the C=S bond. These unusual conversions were carefully studied by computational methods within the DFT framework in order to explain its mechanism and the observed regioselectivity. Thus, they were found to occur as concerted and completely regoselective reactions leading to the (*Z*)-1,3-dithiafulvene isomers **163**, which are kinetically favored [71].



165 **166** **167** (35-92% **168** (80-100%)

R^1 = H, Ph

R^2 = Et, n-Bu, c-pent

Scheme 43. The [3+2]-cycloaddition of 1,2-dithiole-3-thiones **165** with methoxy(phenylethinyl)carbene complex **166** acting as an acetylenic dipolarophile.

5. Conclusions

The presented overview offers an insight in the diversity of reactions, which can be performed with thiocarbonyl compounds by treatment with carbenes and their metal complexes. Depending on the type of thiocarbonyl substrate and nature of the divalent carbon species, diverse processes governed by the reactivity of the initially formed intermediates are observed. Whereas electrophilic carbenes and carbenoids derived therefrom attack the sulfur atom forming in situ reactive thiocarbonyl ylides (*S*-centered 1,3-dipoles), reactions with nucleophilic carbenes tend to occur via carbophilic attack onto the C=S bond and respective zwitterionic species (betaines) determine the further reaction pathways. In analogy to ethylene derivatives [72,73], reactions with strongly electrophilic dihalocarbenes can also occur via asynchronous [2+1]-cycloaddition onto the π-orbital of the C=S bond leading to the formation of reactive diradicals as plausible intermediates. In many

instances, three membered S-heterocycles, i.e. functionalized thiiranes, or ethylenes resulting from their desulfurization are final products. Alternatively, thiirane derivatives can be isolated and desulfurized using known methods. In the case of dihalocarbenes they act in many instances as desulfurizing reagents and gem-dihaloethylenes or even tetrahalocyclopropanes are formed as final products of these reactions. From the point of view of potential practical applications, carbophilic additions of heterocyclic nucleophilic carbenes (NHCs) onto the C=S bond in heterocumulenes are of great importance. Especially in the case of carbon disulfide (CS_2), the obtained stable, zwitterionic hetarylidene dithiocarboxylates are versatile substrates for further exploration not only in organometallic chemistry as superior complexing agents but also in materials and medicinal chemistry. In the case of aryl isocyanates, NHCs can act in their transformations as efficient organocatalysts. Remarkably, despite the fact that nucleophilic heterocyclic carbenes (NHCs) are known to react easily with elemental sulfur yielding corresponding thiones [74], their reactions with thioketones and related thiocarbonyl compounds, e.g. thioesters, have not yet been reported and this might be a challenging problem of the chemistry of this class of carbenes, which have extensively been studied in recent decades [61].

Disclosure statement

No potential conflict of interest was reported by the authors.

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